CHAPTER - III

EXPERIMENTAL TECHNIQUES

Experimental techniques of excitation of band spectra and recording them plays a very important role in the investigation of the spectra of molecules. The probability of obtaining an expected band system depends more or less upon the proper selection of the source to excite it and hence it is essential to know the various spectral sources employed in the production of band spectra. Various types of sources have been used to excite the molecules to produce their band spectra in emission. They range from open flames to large varieties of electric discharges and sophisticated lasers. Among the latter electric arcs, electric spark and a variety of ionic discharges at low pressure are frequently employed.

Many band systems have been observed in flames. Some of them are observed in flames by direct combustion of inflammable substances, others by introduction of additional substances into a flame. Only low-lying electronic states are involved in the transitions producing flame spectra. The energy of the upper electronic state rarely exceeds 5 eV. In flames, excitation occurs mainly as a result of collisions between atoms and molecules. The main disadvantage of the flame source in the production of band spectra is that the substance has to be kept in the gaseous state within the flame.

As the electric arcs produce higher temperatures than flames, they are more suitable for the excitation of spectra of substances whose melting points are very high. The arcs can impart more energy to the molecules and as a result higher energy levels are excited and more number of band systems appears in arcs than in the flames. The arcs in air have been widely used for excitation of spectra of oxides and halides of metals. By enclosing the arc, it may run in an atomsphere of various gases at various pressures. The current density and the material of the electrodes producing the arc are the important factors for the proper excitation of the spectra.

Among the spark sources the uncondensed discharge is commonly used for the production of band spectra. The main disadvantage of condensed discharge is that it also gives rise to a number of atomic lines.

From several years discharge tubes are used very conveniently as a source of exciting the molecular spectra. It offers a large scope of varying the conditions of excitation and also steady condition can be maintained for any desired length of time. The Geissler discharge tubes are most suitable for gases of substances having appreciable vapour pressure at low temperatures. The positive column and negative glow in such discharge tubes are responsible for most of the emission of light and they are utilised for production of the spectra. The main advantage of such sources is greater number of excitated states is possible as compared to arcs and flames.

In the 20th century, due to outstanding achievements of science and engineering, the laser occupies a unique position for the production of band spectra. In fact, in the last two decades new frontiers of lasers i.e. Laser Raman Spectroscopy, Coherent Anti-stokes Raman Scattering (CARS), Lamb-dip spectroscopy, high resolution (Doppler-free) spectroscopy, optogalvanic spectroscopy, two photon spectroscopy, Laser induced fluoresence spectroscopy and other fields appear as thurst fields of research in spectroscopy. Unlike conventional source of light, the laser produces radiation with a high degree of excellence in coherence, monochromaticity, directivity, polarisation and intensity.

However, in the present investigation of the spectra of PbCl and PbO molecules, the high frequency oscillatory discharge tube source was found to be most suitable. The techniques adopted in the present study are described below in detail.

(I) THE DISCHARGE TUBE AND VAC UM SYSTEM

The discharge tubes of conventional type were used as the source. As the melting points of the substance under investigation are high, quartz discharge tubes were employed. Tubes having length about 20 cm and internal diameter between 0.3 and 0.8 cm were found convenient. One end of a tube was provided with a knurling to connect it to a high vacuum pump with a rubber tube. The other end of the tube was sealed with a glass or a quartz window, depending upon the spectral region of investigation. The substance under investigation was kept between the electrodes. The sealing of the joints and fixing of the window were made with Apiezon sealing wax . Two copper foils were wrapped on the tube which would serve as external electrodes.

Continuous evacuation of the discharge tube was done by means of Cenco-hyvac pump which can give an ultimate vacuum of 0.1 micron. A tower containing Sodium hydroxide pellets and an ice-cooled trap were kept in between the discharge tube and the vacuum pump to minimize the contamination of the pump oil caused by vapours from the discharge tube. Both the ends of the discharge tube were kept water-cooled by keeping water soaked cotton-wool near them, so that the vapour of the substance before reaching the transmitting window or pump line of the evacuating system got condensed. The length of the connecting rubber tube in the evacuating system was as small as possible and joints were made leak-proof with araldite. The tube was heated externally with a burner continuously when required to maintain the conditions of the discharge throughout the exposure.

(II) THE HIGH FREQUENCY OSCILLATOR

The high frequency oscillator employed in the present work was fabricated in this laboratory. Fig. 1 shows a schematic diagram of the arrangement used. A variac capable of delivering voltage of the order of 220 volts at 4 amperes is used to regulate the voltage applied to a high tension unit (H.T.). The D.C. out-put voltage is applied to the oscillator (O) and the R.F. out-put power is generated

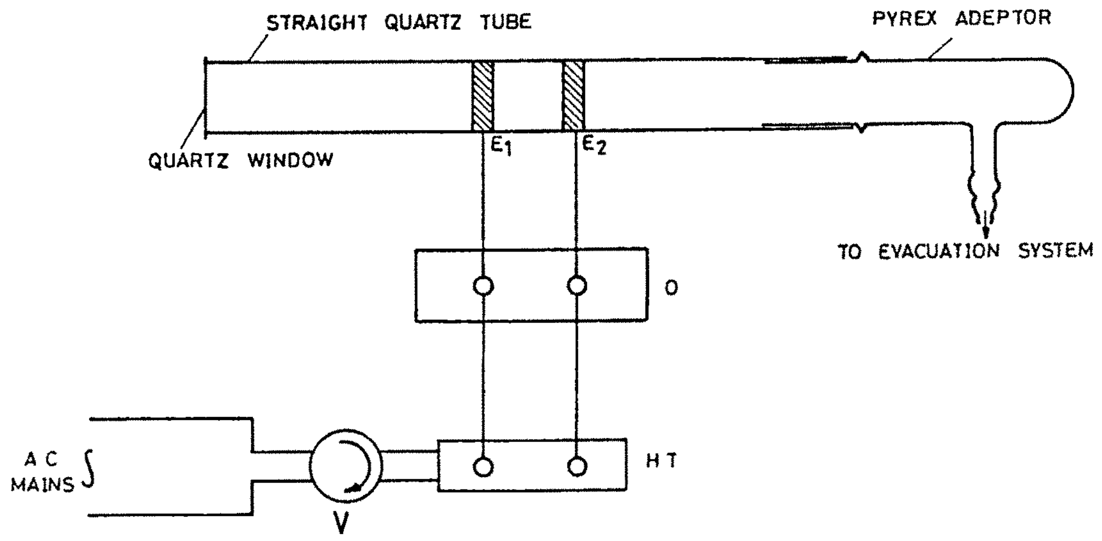


FIG. 1 : SCHEMATIC DIAGRAM OF THE HIGH-FREQUENCY OSCILLATOR AND DISCHARGE TUBE.

which is then fed to the discharge tube by means of external electrodes E_1 and E_2.

(a) HIGH TENSION UNIT

The circuit diagram of the power supply for the oscillator unit is as shown in Fig. 2. The power transformer T_2 delivers 1500-0-1500 volts in its secondary. This output voltage is then rectified by means of two RCA 866 A high vacuum mercury rectifiers. The rectified voltage is filtered using a choke input filter system. A bleeder resistor R_B ($R_1 = R_2 = R_3 = 25000$ ohm) is connected across the outout of the high tension.

(b) THE OSCILLATOR

The oscillator is series fed Hartley push-pull type and is shown in Fig. 3. The two power tubes RCA (811) are connected in push-pull circuit as shown in Fig. 3. A low voltage transformer T_3 delivers 6.3 volts at 4 amperes current suitable for the filaments of the valves. The oscillations are generated in a tank circuit consisting of a variable transmitting type

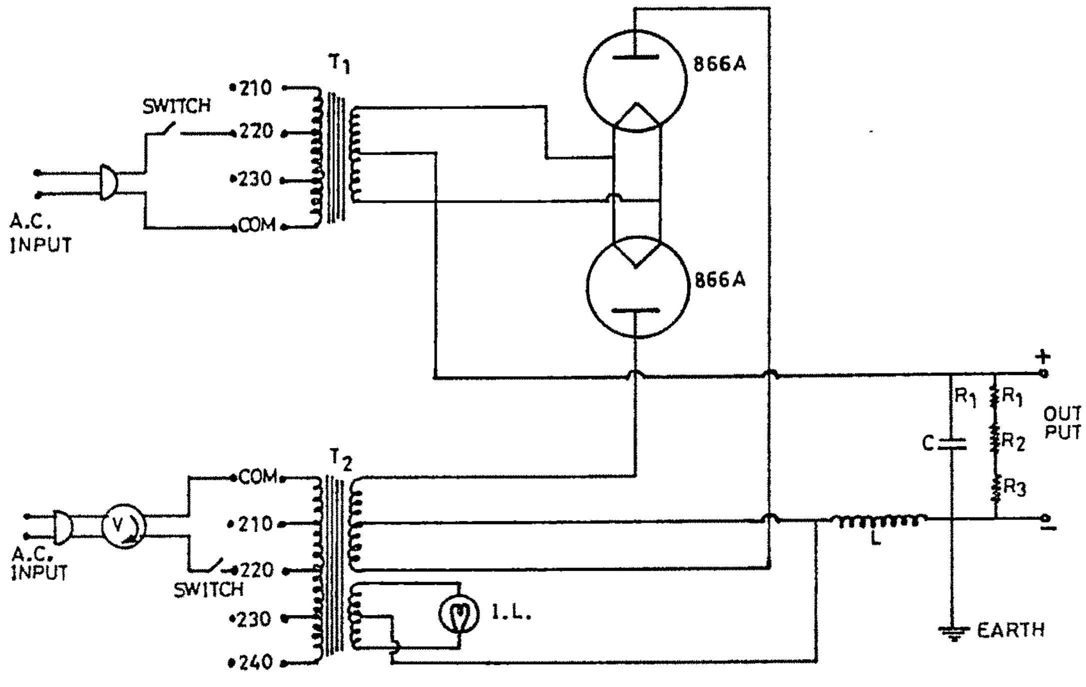


FIG. 2 : CIRCUIT DIAGRAM OF POWER SUPPLY FOR HIGH FREQUENCY OSCILLATOR.

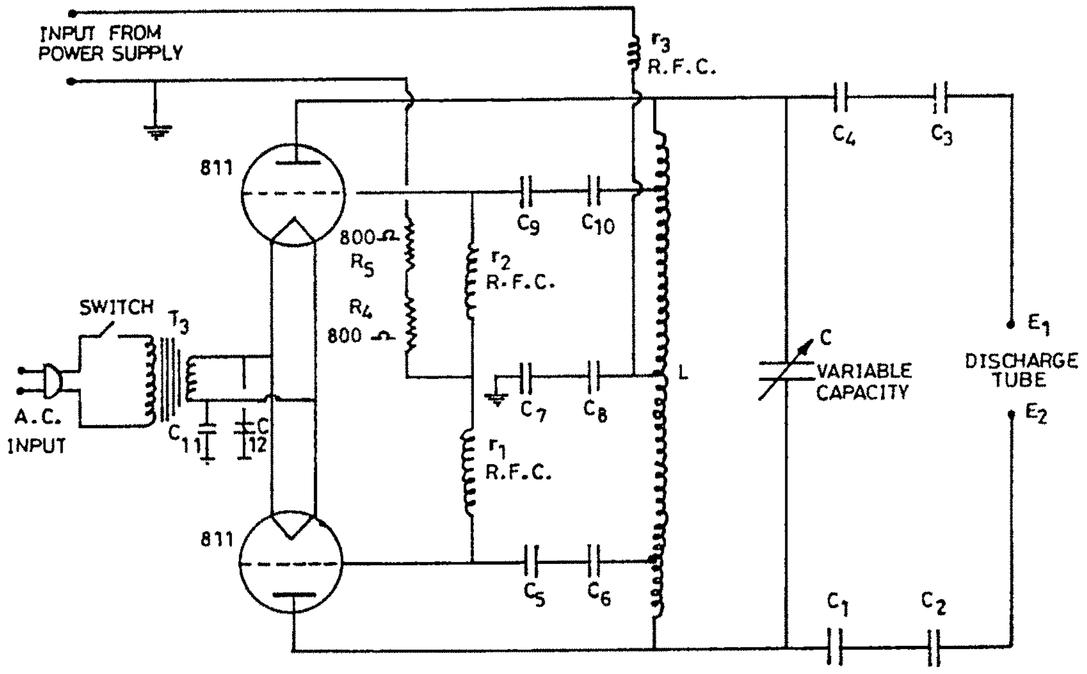


FIG. 3 : CIRCUIT DIAGRAM OF HIGH-FREQUENCY OSCILLATOR.

air-condenser C and an inductance coil L. To vary the frequency, a series of coils with different number of turns and various diameters were prepared. The maximum output was obtained by the proper matching of the coil with the condenser. Thus the oscillator unit is fabricated to give an output of 125 watts at the frequency range 6.5-20 MHz. The oscillator is coupled to the discharge tube at E_1 and E_2 by short and thick copper leads.

Following are the salient features of the high frequency discharge for the study of band spectra.

The molecules in the gaseous state may be excited in a low pressure discharge tube either by electrodes or by electrodeless discharge. The presence of electrodes within the tube causes the 'Life' of a gaseous ions to be short-lived on account of the constants difference of potential between the electrodes. This can be minimised by using the alternating potentials or it may be almost entirely removed by applying the radio-frequency oscillations to the discharge tube by means of external electrodes. The external electrodes are connected to a coil which carries a high frequency current generated by thermionic oscillator valve. The high frequency electric field provides enough electron velocity to excite the molecules of a gas at a low pressure. Electron velocity can be varied by adjusting the field strength and the pressure inside the discharge tube enables to vary the conditions for proper excitation of higher energy levels of the molecules. In fact, the energy available for excitation is governed by the factors such as the pressure inside the tube, the frequency of the oscillator and the voltage across the electrodes.

(III) SPECTROGRAPH

For the present study the spectrograms were taken on Carl-Zeiss two meter plane grating spectrograph in higher orders. The detailed description of the design and working of two meter plane grating spectrograph is given below.

The optical principle of this spectrograph is the Ebert mount of the plane grating with mirror optics. A perspective representation of the path of rays is given in Fig. 4. The rays entering through the slit are rendered parallel by the lower part of the concave mirror and are reflected to the grating. After diffraction produced by the reflection grating, the dispersed rays strike the upper section of the concave mirror, which collects the parallel rays, so that the spectrum is produced in the plane of plate above the grating. The spectrograph has a fine slit which can be narrowed upto nine microns. Attachments are provided for the adjustments of the tilt and height of the spectrum to be recorded.

The grating used in the spectrograph has got a saw-tooth profile and can concentrate the radiation in a preferred angular direction, the position of which depends upon the rake angle of the grating grooves. This special property of the grating is called the "blaze-property" and the rake angle of the grating grooves as the "blaze-angle" of the grating. The grating having blaze angle equal to 5.6° concentrates most of the radiations around 3000 Å in the first order and the grating with blaze angle equal to 10.7° concentrates most of the radiations around 5700 Å whereas the grating with

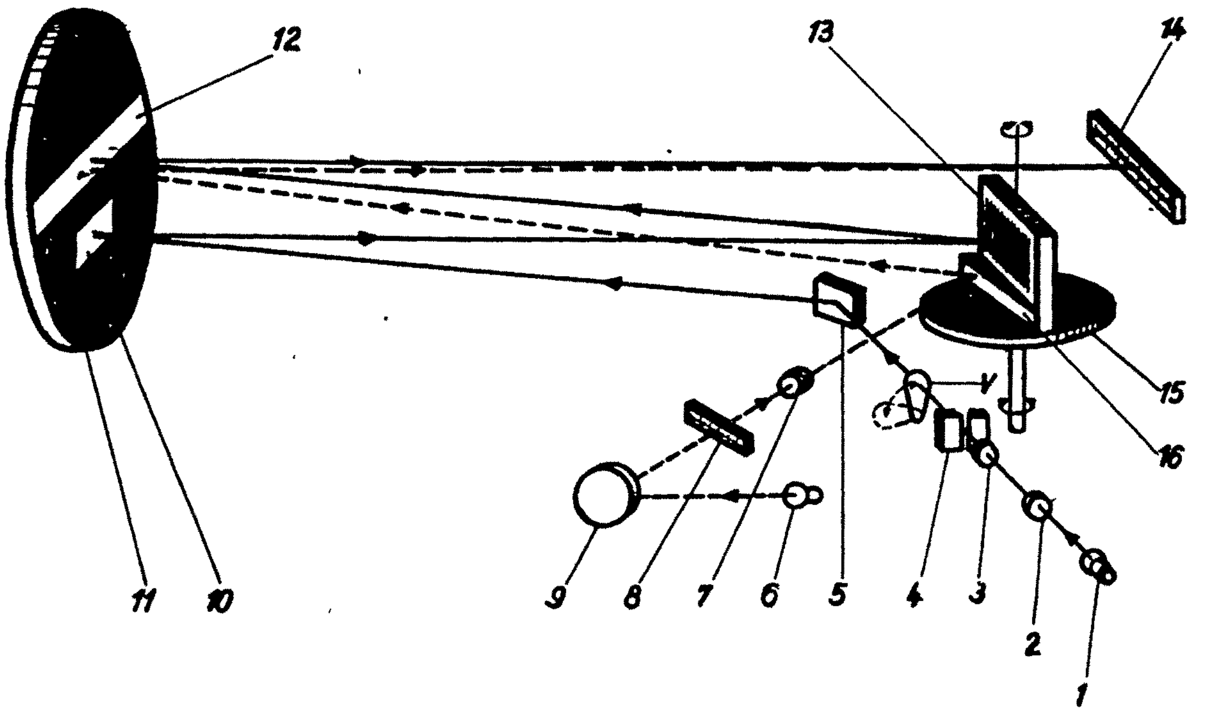


Fig.4 : THE PATH OF RAYS (SINGLE-PASS BEAM) IN PERSPECTIVE IN 2-METER PLANE GRATING SPECTROGRAPH.

1. Source.
2.& 3. Collimating lenses.
4. Slit.
5. Deflecting mirror.
6. Lamp for scale.
7. Lens.
8 Scale.
9. Diflecting mirror.
10. Concave mirror. (lower section)
11. Concave mirror.
12. Concave mirror. (upper section)
13. Plane grating.
14. Plate holder.
15. Grating table
16. Plane mirror.

blaze angle equal to 20.0° concentrates most of the radiations around 10,500 Å. All the three grattings are available in the laboratory having 651 grooves per mm The grating is mounted on a rotatable table and hence it can be set for different wavelength ranges and orders of the spectrum.

The spectrograph has the following outstanding optical properties.

(1) The slit is stigmatically imaged in a 1:1 ratio. Hence the height of the spectrum is exactly the same as the height of the slit.

(2) The mirror system is achromatic i.e. the focussing is independent of wavelength.

(3) The image plane is nearly flat.

(4) The spectrum lines are not curved but they tilt as the grating is rotated. The inclination of the lines can be compensated by tilting the slit in the opposite direction.

(5) The dispersion can be adopted according to the

problem on hand by utilizing the various orders of the grating spectrum. The reciprocal dispersions in the various orders are follow.

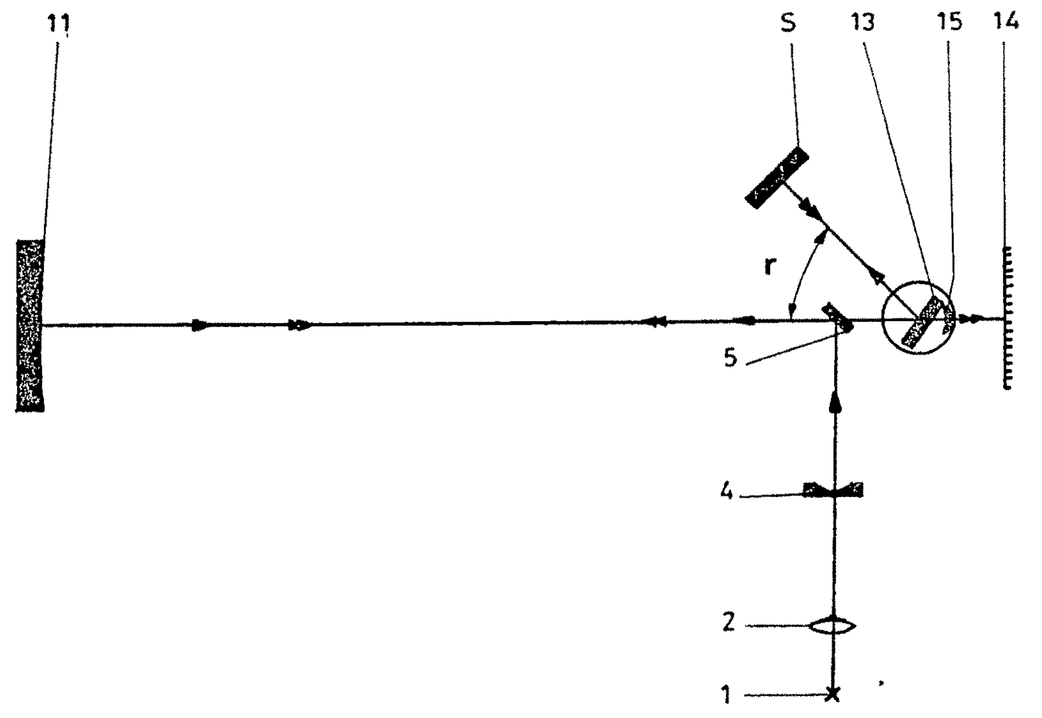
Order	1	2	3	4	5	6	7
Reciprocal dispersion in Å /mm	7.33	3.57	2.27	1.58	1.12	0.77	0.47

(6) The spectrograph is equipped with a supplementary device that enables the rays to impinge on the grating twice. With the utilization of this "double pass" device the dispersion can be doubled. The path of rays in "double pass" is schematically shown in Fig. 5.

The outstanding character of this spectrograph is its high resolving power. The theoretical resolving power is given by the formula

$$R_{th} = m N$$

Where m is the order of the spectrum and N is the total number of grating grooves. For the gratings available in this laboratory with 651 lines per mm the theoretical first order resolving power is



<u>FIG. 5</u> : SCHEMATIC DIAGRAM OF PATH OF RAYS IN DOUBLE PASS BEAM.

1. Source
2. Collimating lens
4. Slit
5. Deflecting mirror
S Plane mirror

11. Concave mirror
13. Plane grating
14. Plate holder
15. Grating table

45,600. The practical resolving power $\lambda/d\lambda$ is somewhat less than theoretical value. This high resolving power of the grating was of a great advantage in the present investigation and helped to resolve the close structure of rotational lines due to isotopic effect.

While recording the spectrum appropriate filter or a predisperser was used to avoid the overlapping of the other unwanted different order spectra.

(4) COMPARISION SPECTRUM AND MEASUREMENT

For obtaining the wavelength data of the spectrum under investigation, a comparision spectrum of iron arc running at 110 volts at 4 amps., was recorded in juxtaposition with it. The iron spectrum is extensively used for comparision because of the convenience and simplicity associated with it in addition to the fact that it gives large number of lines in the visible and ultraviolet regions of the spectrum.

The iron secondary standards adopted by

international astronomical union 1928, 1932 and 1938 (Sawyer 1944) were selected from Hilger charts (Hilger and Watts, London). The M.I.T. wave length table (Harrison 1939) was occasionally used.

The measurements of the plates were carried out on an Abbe comparator having a least count of one micron.

For the wavelength determination of the grating spectra, a standard line whose wavelength λ_m at X_1 was known, was selected from the reference spectrum. The wavelength of the unknown line or band head at X was determined by substituting in the following formula.

$$\lambda_m (X) = \lambda_m (X_1) \pm \Delta x \, D_m (X_1 + X)/2$$

where $\Delta x = X_1 - X$

= distance between the known line $\lambda_m (X_1)$ and the unknown line $\lambda_m (X)$ and

$D_m (X_1 + X)/2$ is the reciprocal liner dispersion midway between the two lines. The formula is accurate for a distance $\Delta x \simeq 20$ mm and correction was applied for larger distances. Measurement of sharp lines is accurate within ± 0.05 cm^{-1}.

(5) MICRO-DENSITOMETER AND PHOTOMETRIC RECORDER

Intensity records of rotational lines of PbCl and PbO molecules were taken on Carl-zeiss Microdensitometer G II coupled with potentiometric recorder G_1B_1. These records not only give the intensity distribution of lines in various branches but also help in picking up the branches while attempting the rotational analysis. The detail of working of microdensitometer and the potentiometric recorder is given below.

The microdensitometer G II with movable plate stage has been mainly used for photometric measurements of emission spectra.

The high intensity light source of the microdensitometer, transilluminates the spectrogramme to be recorded and the light that is transmitted by the plate is received by the Selenium photovoltaic cell. The voltage produced by the selinium cell which is proportional to the light intensity received; is measured by the sensitive mirror galvanometer. The output of the microdensitometer is fed to the potentiometric recorder G_1B_1 coupled with it by radio-frequency cable . The whole system is shown in Fig. (6).

In addition to the built in vacuum photoemissive tube, a normal Selenium photovoltaic cell is attached to the photocell housing and connected to the mirror galvenometer. The plate stage driven by the recorder through a recording shaft is to be connected to the microdensitometer. Various speeds to run the plate stage as well as the paper on the recorder are available. The high paper speed coupled with low plate stage speed gives finer details of intensity and spacing of rotational lines in a band.

(6) PLANIMETER FOR THE MEASUREMENT OF AREA UNDER THE PEAK OF A SPECTRAL LINE

Introduction

To calculate the rotational temperature of the source emitting the spectrum of PbO molecules,

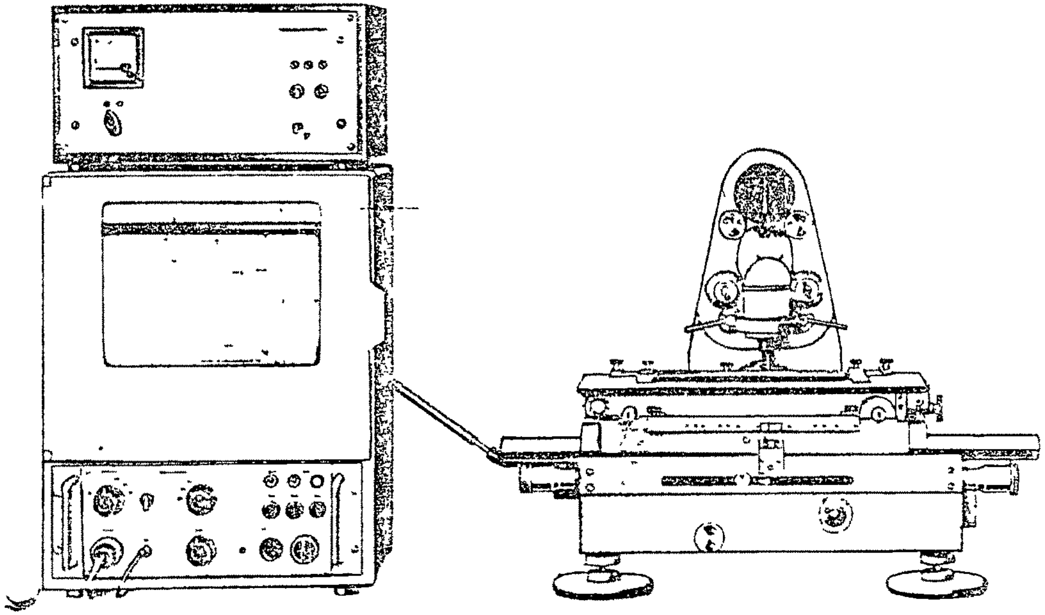


FIG. 6 : MICRODENSITOMETER G-II COUPLED WITH POTENTIOMETRIC RECORDER G1 B1.

graph of $\ln (I_{em}/2K) \longrightarrow K(K-1)$ is plotted. But I_{em} is proportional to the area under a peak and hence area under each peak has to be measured very accurately. There are several ways to determine the area of irregular figures on a plane. Some of them are given below.

(1) Averaging of ordinates.
(2) Empirical Rules.
  (a) Trapezodial method.
  (b) Simpson's Rule.
  (c) Durand's Rule.
(3) Cross section paper.
(4) Weighing.
(5) Mechanical Integrators.

There are many types of integrators, called Planimeters used for determination of area very accurately. The most common of them is the "Polar Planimeter" which is used in this laboratory.

It is an extremely accurate robust in construction designed to stand up the wear and tear of daily intelligent use for greater life. This is generally used by Architect engineers and scientific workers.

DESCRIPTION OF THE INSTRUMENT

The instrument depicted in Fig.7 is of adjustable arm type. It consists of two arms. The tracing arm carries a sharp tracing point. It is passed round the outline of the figure whose area is to be measured. The tracer arm has a carriage which is adjustable to the various positions. The carriage has a wheel rigidly attached to it. The wheel has a circumferencial scale which is divided into 100 equal parts. By means of a vernier, each of the above parts may be subdivided into 10 equal parts. Connected to the shaft of the wheel, by means of a small worm is a recording disc. The recording disc is divided into 10 equal parts. Each division of the disc indicates one complete revolution of the wheel. The readings on the disc are indicated by means of a pointer. The tracing point is also provided with a handle and an adjustable support so that the tracing pin would not dig into the paper. At one end of the pole arm is a sphere which rests in a socket on the carriage and thus partly controls

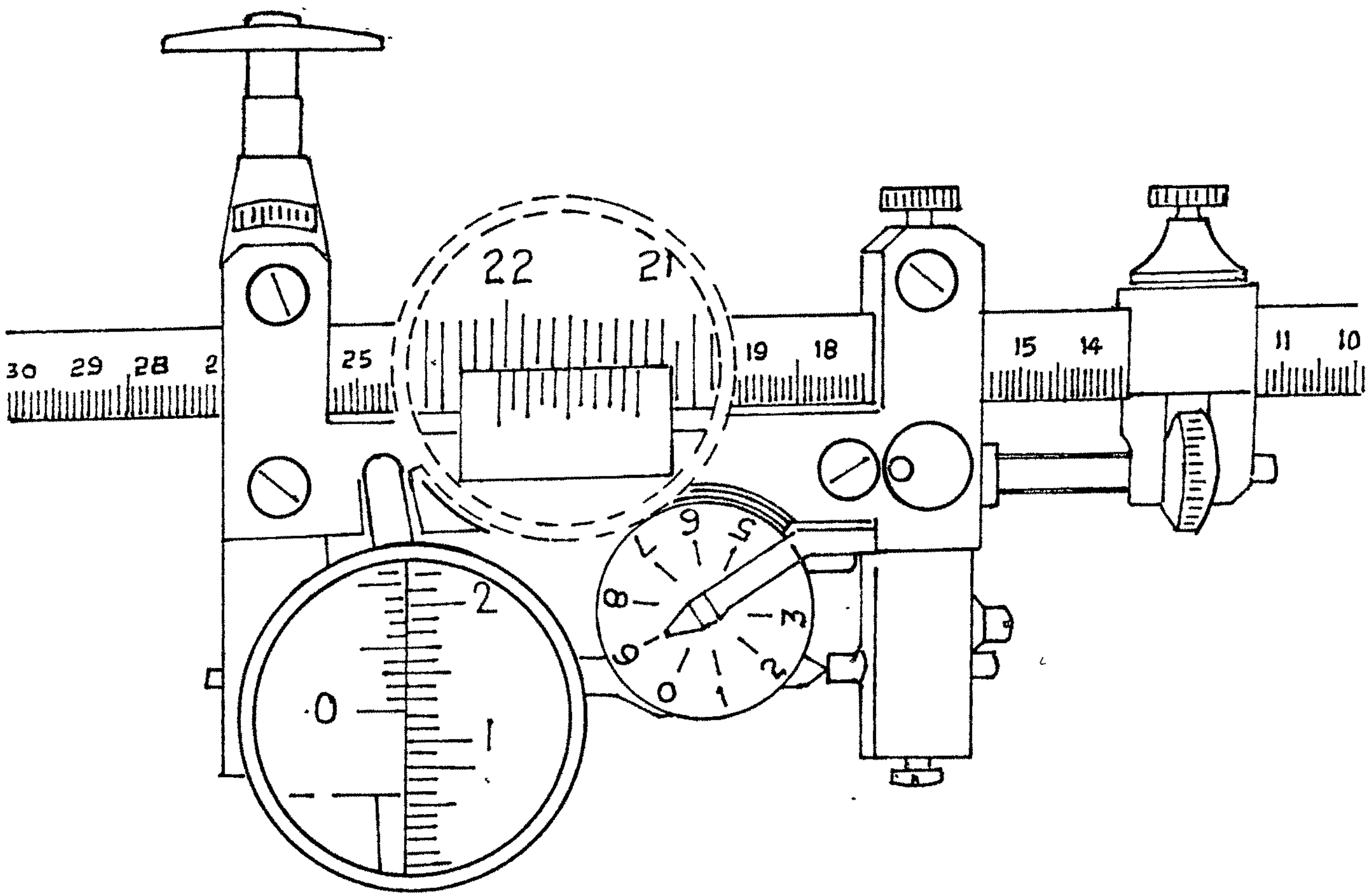


Fig. 7

Sketch diagram of planimeter

its movement when area is being traced. On the other end is a needle pointed weight in operation. The entire instrument pivots about this point.

The readings for measuring the area consist of two parts

(a) The complete rotational shown by the counting dial.

(b) The partial rotation shown by the measuring wheel itself. The figures and sub-divisions giving tenths and hundredths of rotational respectively, and finally the vernier reading the thousands provide an accuracy of measurement upto ± 0.0001 cm.

MINIMISING ERROR OF MEASUREMENT

(1) Place the balancing weight in such a position that neither the tracing point nor the record wheel be lifted from the paper.

(2) Adjust the length of the tracing point so that it almost touches ore paper but will not dig into it.

(3) Make a rough swing of the tracing point over

the figure to see that the angle between the two arms becomes very small at any position. If it does, it may become difficult to trace the figure smoothly. Hence the fixed point should be relocated.

(4) When the figure is traced, the record wheel may go off the paper on which the figure is drawn. Since this may give an incorrect reading, the fixed point should be re-located. If re-location is not satisfactory the figure should be subdivided into two or more small areas and each area be measured separately.

(5) Make two or more tracings of the figure until a substantial agreement of the readings is obtained. The closeness of the readings required for satisfactory accuracy is a function of the size of the figure. A variation of 0.005 sq. inch in the reading of 5 sq. inch figure represents 0.1% variation of the total area.

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